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Optical Activity Measurement of Amino Acid Films by Circular Dichroism Spectroscopy

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The origin of homochirality in terrestrial biomolecules (L-amino acid and D-sugar dominant) remains one of the most mysterious problems in the research for the origins of life. Rational explanations for the chiral asymmetry introduction into biomolecules are required through interdisciplinary collaborations. One of the most attractive hypotheses in the context of astrobiology is “Cosmic Scenario” as below [1, 2]; (1) Asymmetric reactions of prebiotic molecules on interstellar dust surfaces in molecular cloud circumstances were introduced by asymmetric radiation sources in space, that is “chiral radiations”. (2) The chiral products were transformed into the complex organic materials including amino-acid precursors as “chiral seeds”. (3) The complex organic materials as “chiral seeds” were transported with meteorites or asteroids to primitive Earth resulting in terrestrial biomolecular homochirality.

Several ground experiments to validate the scenario have been investigated asymmetric photochemical reactions in simple biochemical molecules using circularly polarized light (CPL) from high-energy particle accelerators [3]. Presently, we are carrying out irradiation experiments by using CPL with different wavelengths to investigate the photon energy dependence of photochemical chiral reactions [4]. As for the sample, we formed thin solid films of racemic mixture of alanine on quartz substrates from crystal powders of DL-alanine by using a thermal-crucible vacuum-evaporation system in HiSOR. The thin solid films of racemic mixture of alanine were irradiated of L- or R-CPL in different wavelengths using the undulator beam line BL1U of UVSOR-III [5]. In case of CPL irradiation in shorter wavelengths than 200 nm, the samples were set in a vacuum sample chamber preventing attenuation by air absorption. On the beam entrance side of the vacuum sample chamber, a gate valve with an MgF_2 vacuum sealing window was mounted. The irradiated CPL wavelengths were 180 and 155 nm corresponding to photon absorption bands of alanine molecule. The total doses of irradiated photon energy were measured with photoelectron current of a silicon photodiode (International Radiation Detectors, Inc.) settled at the sample position.

Circular dichroism (CD) spectra of the CPL irradiated films were measured at beam line BL-12 of HiSOR to clarify the optical activity emergence by CPL irradiation. CD spectroscopy can detect optical activity with a high accuracy because CD spectra sensitively reflects the steric structures of chiral molecules. Fig.1(a) and (b) are CD spectra of DL-alanine films irradiated by L- or R-CPL at 180 nm and 155 nm in wavelength, respectively. In order to delete the effects of linear components, the CD spectra at sample rotation angles (0, 45, 90, and 135 degrees) were individually measured and averaged them. The observed spectral profile strongly depends on the irradiated CPL wavelength and the polarization (L- or R-CPL) [6]. The measurement and theoretical calculation of CD spectra of L-alanine molecule has revealed that the chromophores such as carboxyl and amino groups are derived from the characteristic electronic transitions (π-π^* and n-σ^*) corresponding to the wavelengths as shown on Fig.1(c) [7, 8]. It is strongly suggested that optical activity emergence depends on photon energy of the irradiated CPL. Detailed analysis of CD spectra is in progress supported by quantum chemical calculations.

Presently, we are also planning the further irradiation experiment using CPL at 121.5 nm in wavelength, which is corresponding to hydrogen Lyman-alpha line. The clarification of full mechanism of the optical activity emergence potentially has relevance to the origin of terrestrial bioorganic homochirality stimulated by “chiral photon radiation”.

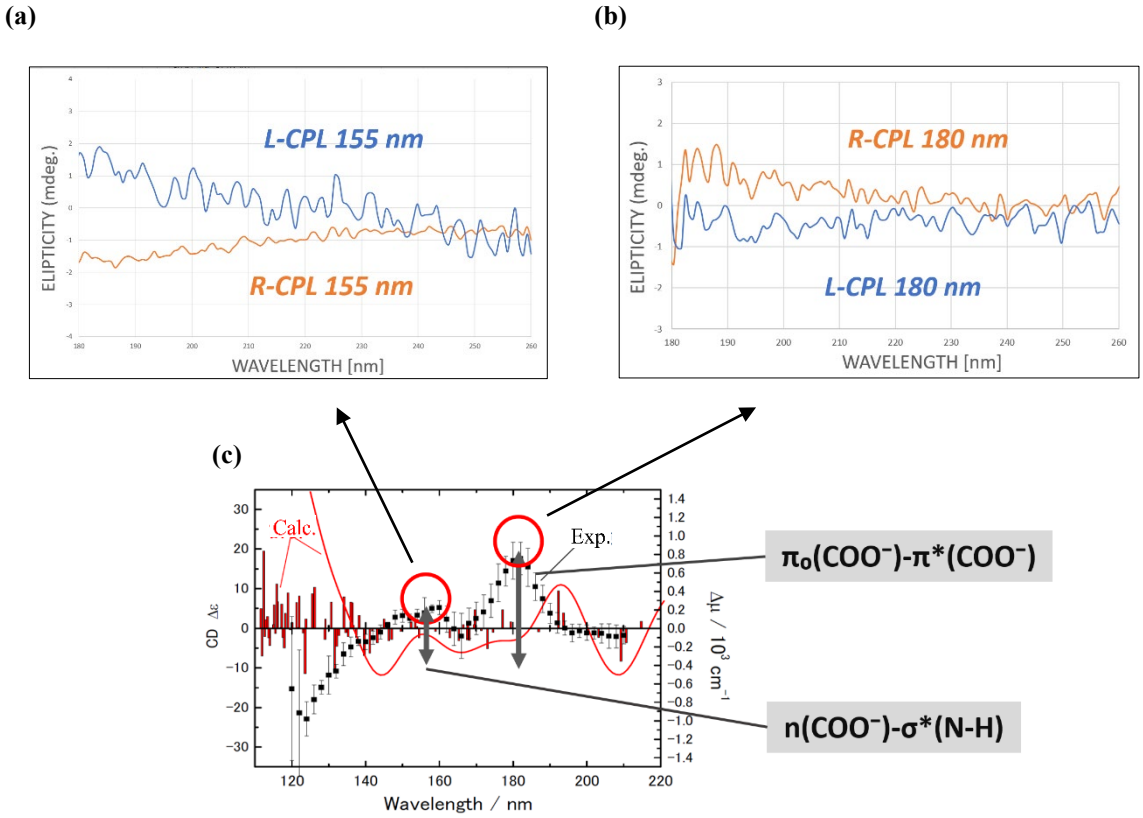

FIGURE 1. CD spectra of the L- or R-CPL irradiated DL-alanine films measured at BL-12 of HiSOR. The CPL irradiation wavelengths were (a) 155 nm and (b)180 nm at BL1U of UVSOR-III. (c) The measured and theoretical calculated CD spectra of L-alanine molecule [7, 8].

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